# Effect of Maceral Composition and Vitrinite Reflectance on the Combustion Behavior of Six hvA Bituminous Coals

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## Introduction

A common way of classifying coals is by rank, that is, according to the degree of metamorphism, or progressive alteration of the plant debris as it is transformed into the natural series from lignite to anthracite.. In the United States the rank classification system was established by the American Society for Testing and Materials (ASTM), and is based on the percent volatile matter and fixed carbon obtained from the proximate analysis and on a dry, mineral-matter-free basis, and the heating value in British thermal units per pound (Btu/lb) expressed on a moist, mineral-matter-free basis.(1) Each rank of coal from lignite to anthracite has distinctive chemical and physical characteristics which influence the behavior in a given application. This rank classification is commonly used as a guide in the selection of pulverized coal for use in utility and industrial boilers. Although rank can indicate, in some cases, general processing behavior, it is not sufficient to characterize the specific behavior of a coal under specific utilization conditions. This derives, at least in part, from the fact that different maceral compositions for coals of the same rank can give rise to different properties, and hence, different behavior during processing. Therefore, assessment or prediction of processing, particularly combustion, behavior based on rank alone is not reliable. In higher rank coals, however, where the differences between macerals is less significant,(2) the behavioral differences as a consequence of maceral compositon are less significant.

Due to the relatively high vitrinite concentration in American coals, their chemical analyses tend to reflect the composition and properties of the vitrinite. Therefore, the parameters used to classify coals according to rank often reflect the rank of the vitrinite. Further, the characteristics of vitrinite are considered to change in a fairly uniform manner throughout the coalification series. One characteristic of vitrinite which can be measured easily is its reflectance. It is a measure of percent light reflected from a polished surface of coal. Because the degree of petrographic heterogeneity is much greater in lignites than in coals of higher rank, there are some difficulties in determination of vitrinite reflectance in these coals.

It has been observed in practice that a switch from a familiar coal can lead to a change in the amount of unburnt carbon in the fly ash from a utility boiler. There are many possible explanations for this, but in recent years increasing attention is being focussed upon the maceral composition of coals as being a contributor to the problem. From the available published work, relationships between certain petrographic properties and coal combustion behavior can be inferred. In particular, inertinite macerals appear to bum less readily than the so-called "reactive macerals".(3,4) Thus, coals with high inertinite contents may require high temperature and/or long residence time to avoid high unbumt carbon loss. This is supported by results from laboratory experiments and some industrial experience.(3-8) The purpose of the current work was to determine the effect of maceral composition and vitrinite reflectance on the combustion behavior of six maceral-rich hvA bituminous coals.

## Experimental

Combustion experiments were conducted in an entrained-flow reactor, a schematic diagram of which is given in Figure 1. The system is composed of a preheater, water-cooled feed probe, cyclone, water-cooled collector probe and char collector. A stream of coal particles was fed by the screw feeder and entrained in a primary gas stream at ambient temperature, then passed through a water-cooled probe and injected at the top of a hot cylindrical reaction chamber, which was maintained electrically at a specified reaction temperature. At the same time, a secondary and larger stream of carrier gas, which was preheated to the reactor temperature, was isokinetically injected around the primary gas stream in laminar flow to ensure that the particles were not dispersed radially to the furnace walls. A ceramic disk was placed above the injector tip to serve as a flow straightener. The secondary gas temperature was adjusted so that upon mixing of the primary and secondary gases the combined gas stream attained the desired reaction temperature. Heating elements around the reactor produced a uniform wall temperature. The estimated heating rate of the particles is $10^3$ to $10^4$ K/sec. The entrained coal particles travelled in a pencil-like stream down the axis of the reactor. The products of combustion were collected through a water-cooled collector probe that quenched reactions. Solid products (chars) were collected in the cyclone, condensible liquids (tars) were deposited on the filter, and gaseous products were released into an exhaust stack. Detailed design specifications and description of the ancillary equipment are presented elsewhere.[9-11]

In this study, six maceral-rich hvA bituminous coal samples were selected from the D.O.E/Penn State Coal Sample Bank. The selection was based primarily on differences in maceral composition and vitrinite reflectance. The coals were divided into two groups: one group of three having similar maceral composition but different vitrinite reflectance, and the other group having similar vitrinite reflectance but different maceral composition. Full analyses of the six samples are shown in Table 1. By way of example PSOC-1501 is referred to as a low-reflectance, vitrinite-rich coal and PSOC-1374 as a high-reflectance, vitrinite-rich coal of the same rank. A similar relationship holds for PSOC-296 and PSOC-733 (liptinite-rich coals), and PSOC-861 and PSOC-736 (inertinite-rich coals). Three particle size fractions of the six coals, with mean particle diameters of 63, 90, and 127 μm, were prepared and used in this study.

The samples were partially combusted in the reactor at temperatures of 1073 and 1273 K and residence times of typically less than 0.3s. Coal particle residence times in the furnace were determined using a computer flow model. The governing equations and principles of this model have been discussed elsewhere.[7,12] The isokinetic velocity was 128 cm/sec for both the primary and secondary gases. Prior to an experiment the temperature profiles in the reactor were determined using a suction pyrometer. The sample collector probe was then positioned in the reactor, and the coal feeder calibrated to deliver 0.5 g/min.

Proximate analyses of the coals and resulting char samples were obtained using a Leco MAC-400 proximate Analyzer. Weight loss due to the partial combustion was calculated by using ash as a tracer. On a dry, ash-free basis the governing equation is:

$$\Delta W = 100\% \left[ 1 - \frac{A_0\,(100 - A_1)}{A_1\,(100 - A_0)} \right]$$

where $\Delta W$ is the calculated weight loss on a dry, ash-free basis; $A_0$ is the proximate ash content of dry coal; and $A_1$ is the proximate ash content of dry char. An assumption in this calculation is that mineral matter in the coal does not undergo transformations during pyrolysis which would change the quantity of ash produced upon ashing the chars.

## Results and Discussion

The terms "reactives" and "inerts" as used in the coke industry will be used throughout this work. The prediction of weight loss, according to the concentration of reactive macerals, would be as follows:

| | |
|---|---|
| For the low vitrinite reflectance group, | PSOC-1501 > PSOC-296 > PSOC-861 |
| For the high vitrinite reflectance group, | PSOC-1374 > PSOC-733 > PSOC-736 |

The two vitrinite-rich coals (PSOC-1501 and PSOC-1374) and a liptinite-rich coal (PSOC-296) would be considered as reactive coals, whereas the two inertinite-rich coals (PSOC-861 and PSOC-736) would be considered as less reactive.

The effect of residence time over the range 0.1 to 0.3s on the weight loss during combustion of 100x140 mesh particles of the low and high vitrinite reflectance coals at 1073 K is shown in Figures 2 and 3, respectively. Despite having similar volatile matter contents and ASTM rank, the figures shows that the weight loss by the reactive coals (PSOC-1501 and PSOC-1374) is much higher than those of the inertinite-rich coals (PSOC-861 and PSOC-736). The concentration of reactive macerals for PSOC-1501 and PSOC-1374 were 93.9 and 95.1% compared to 61.7 and 34.9 % for the inertinite-rich PSOC-861 and PSOC-736 coals, respectively. The lower weight loss by the inertinite-rich coals is a consequence of the more aromatic nature of the inertinites. In addition, vitrinite and liptinite contain more oxygen and hydrogen, respectively, than inertinite and are thus likely to be more reactive than inertinite.

As is shown in Table 1, PSOC-296 and PSOC-733 have considerable amounts of inert macerals, 32.4% and 29.1%, respectively. Therefore, it might be expected from the maceral compositions that the weight loss of these two coals would lie between those of the vitrinite-rich and inertinite-rich coals. This can be seen for PSOC-733 in Figure 3. However, despite the relatively high inert content of PSOC-296, both vitrinite-rich PSOC-1501 and liptinite rich PSOC-296 have similar weight losses as seen in Figure 2. Based only on the reactive maceral content, therefore, the difference in weight loss behavior is much smaller than might be expected. This indicates that, during the initial stages of combustion, the concentration of inert macerals seems to have much less influence than the liptinite content. A high liptinite concentration enhances ignition, due in part to the relatively higher hydrogen content. As the H/C atomic ratio of the coal increases, ignition of the volatiles is promoted, thereby increasing the weight loss rate. A comparison of the H/C atomic ratios of the coals shows that liptinite-rich PSOC-296 has a higher H/C atomic ratio (0.83) than vitrinite-rich PSOC-1501 (0.79), Table 1. A general trend is that the low vitrinite reflectance coals (PSOC-1501, PSOC-296, and PSOC-861) tend to have higher H/C ratios than the high vitrinite reflectance coals (PSOC-1374, PSOC-733, and PSOC-736).

The effect of residence time over the range 0.1 to 0.3son the weight loss during combustion of 100x140 mesh particles of the low vitrinite reflectance coals at 1273 K is shown in Figure 4. A comparison with Figures 1 and 3 shows that as temperature is increased the effect of maceral composition on weight loss is decreased.

Figure 5 shows the effect of residence time on the weight loss of 140x200 mesh particles of two vitrinite-rich coals (PSOC-1501 and PSOC 1374) during combustion at 1073 K . The vitrinite reflectance values for PSOC-1501 and PSOC-1374 are 0.73 and 0.89, respectively. As can be seen the low vitrinite reflectance coal showed a higher weight loss. A similar trend was observed in Figure 6 for the inertinite-rich coals PSOC-861 and PSOC-736 with vitrinite reflectances of 0.73 and 0.95, respectively.

The effect of particle size on the weight loss during combustion at 1073 K and 0.1-0.3s residence times is shown in Figures 7 through 10. Figure 7 shows the effect of particle size on the weight loss of PSOC-733. The smaller particles experienced greater weight loss than the larger ones at all residence times. Figure 8 shows a similar trend for the inertinite-rich PSOC-736. Because these coals have a considerable concentration of inert maceral, they are not likely to swell significantly. Therefore, the initial particle size will be the effective size and the weight loss will be related to the initial size. As the data in Figures 7 and 8 indicate, physical factors such as particle size may be important in determining weight loss for the less reactive (inertinite-rich) coals.

The effect of particle size is less well defined for the reactive coals. Figures 9 and 10 show the effect of particle size on the weight loss behavior of vitrinite-rich PSOC-1501 and liptinite-rich PSOC-296 during combustion at 1073 K. The curves in Figures 9 and 10 show similar trends to those observed by Tsai.[7] In both cases, the weight loss behavior was rather insensitive to particle size. Since these coals are considered to be highly reactive, the observed results may be due to their thermoplastic properties. The degree of swelling for these reactive coals is larger than for the inertinite-rich coals and higher concentrations of reactive macerals are thought to change the thermal response of the coal. Thus, the effective particle size for the reactive coals during reaction will be greater than that of the initial particle size. Because particle size changes will affect the time-temperature history of the coal particles, which in turn controls to some extent their behavior in the reactor, the weight loss behavior will vary accordingly.

The ignition delay time is dependent on the gas temperature and particle size. At short residence times (prior to ignition), where the weight loss is due to devolatilization, smaller particles of the reactive coals show higher weight loss, Figures 9 and 10. In larger particles, on the other hand, the escape of volatiles from the coal matrix is retarded, and hence weight loss is reduced. At longer residence times (after ignition), however, the weight loss by the larger particles gradually increases, until the weight loss for all paricle sizes become similar. This may be due to the influence of slip velocity on the mixing of the volatiles and the oxidant at the particle surface, or due to a more reactive char.

## Summary and Conclusions

The experimental results indicate that the six hvA bituminous coals studied displayed different behavior during combustion. This was attributed to differences in maceral composition and rank as measured by vitrinite reflectance. Vitrinite-rich and liptinite-rich coals lost more weight than inertinite-rich coals under similar experimental conditions. No significant differences in weight loss were observed between vitrinite-rich and liptinite-rich coals. A lower weight loss rate is believed to be characteristic of high inertinite contents. This is probably due to the existence of high aromaticity and strong cross linkages which exist within the inertinite macerals. For coals with similar maceral compositions, although the weight loss decreased with increasing vitrinite reflectance, there was not a direct and simple correlation between the weight loss and vitrinite reflectance.

Although some smaller particles showed higher weight loss than larger particles of the same coal under similar experimental conditions, there was not a general relationship between the weight loss and the initial particle size. While the weight loss by the less reactive coals (inertinite-rich coals) was sensitive to particle size, the weight loss by the reactive coals (vitrinite-rich coals) was independent of particle size.

In summary, for the high volatile bituminous coals, rank as measured by mean maximum vitrinite reflectance and maceral composition must be considered together with ASTM rank when predicting combustion behavior.

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## Table 1

## Analytical Data for the Coal Samples Used

| Sample No | PSOC-1501 | PSOC-296 | PSOC-861 | PSOC-1374 | PSOC-733 | PSOC-736 |
|---|---|---|---|---|---|---|
| **Proximate Analysis: (wt%)** | | | | | | |
| % Moisture | 5.80 | 4.18 | 3.66 | 6.76 | 1.75 | 3.23 |
| % Ash(dry) | 5.55 | 18.19 | 10.93 | 8.82 | 21.44 | 8.59 |
| % Volatile Matter(daf) | 43.07 | 44.26 | 38.10 | 36.37 | 34.20 | 28.12 |
| % Fixed Carbon (daf) | 56.93 | 55.74 | 61.90 | 63.63 | 65.80 | 71.88 |
| **Ultimate Analysis: (wt%, daf)** | | | | | | |
| % Carbon | 80.49 | 82.09 | 82.65 | 84.77 | 84.81 | 86.70 |
| % Hydrogen | 5.27 | 5.70 | 5.42 | 5.55 | 5.36 | 4.88 |
| % Nitrogen | 1.55 | 1.82 | 1.18 | 1.58 | 1.44 | 1.40 |
| % Total Sulfur | 0.68 | 1.20 | 0.83 | 0.80 | 1.31 | 0.62 |
| % Oxygen (Diff) | 12.01 | 9.19 | 9.92 | 7.30 | 7.08 | 6.40 |
| **Maceral Composition: (vol%, dmmf)** | | | | | | |
| Vitrinite | 92.4 | 41.4 | 60.5 | 93.3 | 48.1 | 24.2 |
| Fusinite | 1.9 | 8.3 | 5.4 | 2.2 | 2.6 | 8.2 |
| Semifusinite | 2.4 | 7.9 | 30.9 | 1.2 | 19.7 | 47.0 |
| Macrinite | 0.5 | 2.1 | 1.0 | 0.2 | 1.4 | 1.9 |
| Micrinite | 1.2 | 14.1 | 1.0 | 1.3 | 5.4 | 8.1 |
| Sclerotinite | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Sporinite | 1.4 | 23.6 | 1.1 | 1.8 | 20.2 | 10.7 |
| Resinite | 0.1 | 2.5 | 0.1 | 0.0 | 2.5 | 0.0 |
| Alginite | 0.0 | 0.2 | 0.0 | 0.0 | 0.2 | 0.0 |
| **H/C: (Atomic Ratio)** | 0.7868 | 0.8334 | 0.7880 | 0.7863 | 0.7589 | 0.6760 |
| **Mean-Max Vitrinite Reflectance ($R_0$): (%, in oil)** | 0.73 | 0.74 | 0.73 | 0.89 | 0.94 | 0.95 |
| **Description** | low-reflectance vitrinite-rich | low-reflectance liptinite-rich | low-reflectance inertinite-rich | high-reflectance vitrinite-rich | high-reflectance liptinite-rich | high-reflectance inertinite-rich |

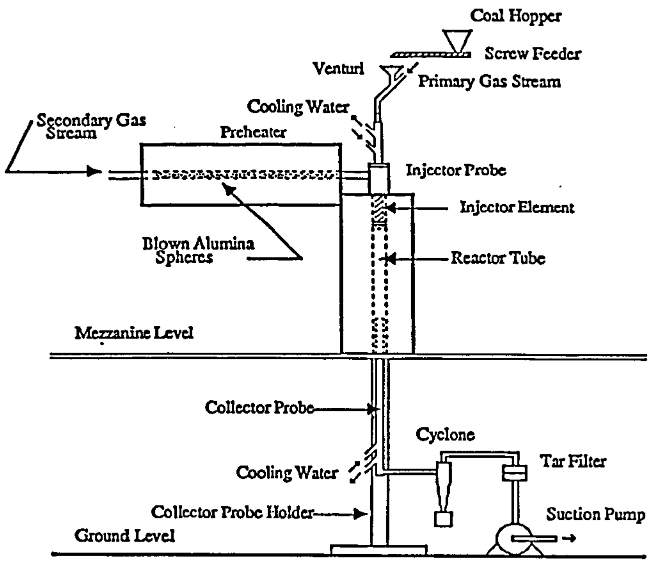


**Figure 1. Configuration of Entrained-Flow Reactor and Ancillary Equipment**

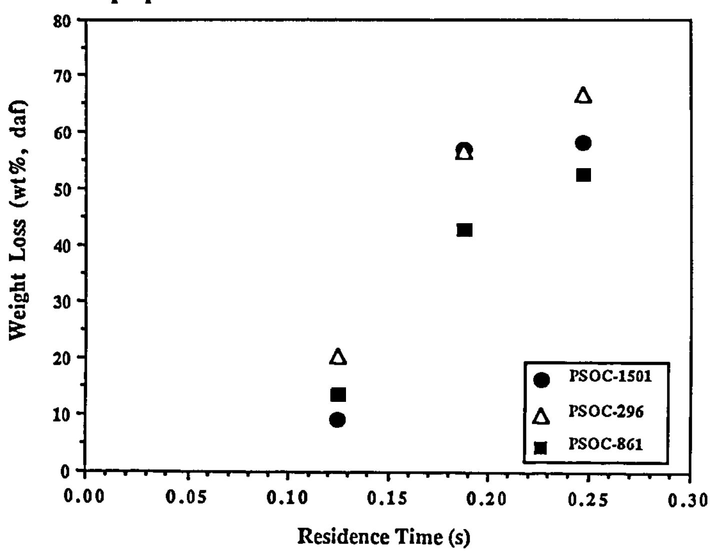


**Figure 2. Effect of Maceral Composition on Weight Loss During Combustion of 100x140 Mesh Fraction of Low Vitrinite Reflectance Coals at 1073 K**

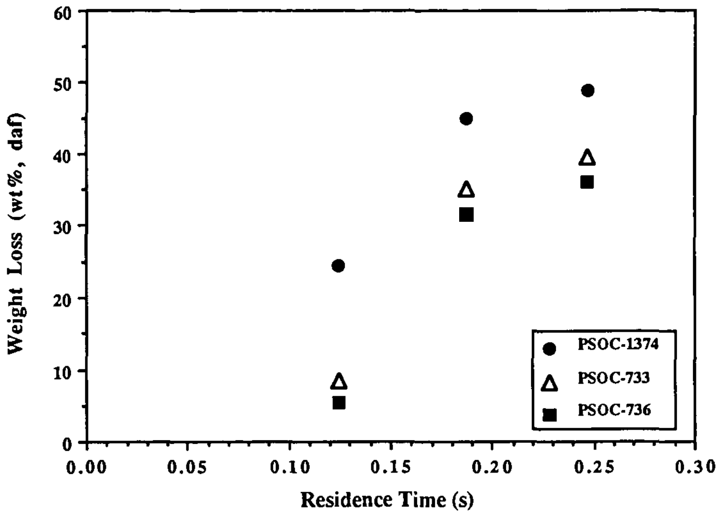


**Figure 3. Effect of Maceral Composition on Weight Loss During Combustion of 100x140 Mesh Fraction of High Vitrinite Reflectance Coals at 1073 K**

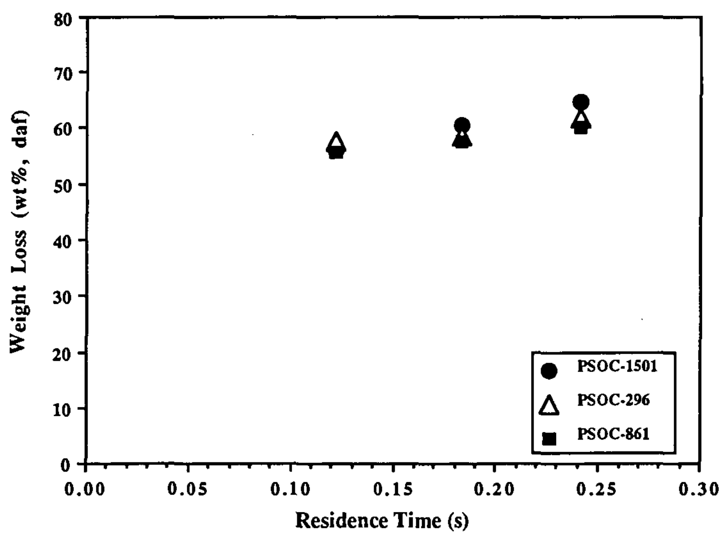


**Figure 4. Effect of Maceral Composition on Weight Loss During Combustion of 100x140 Mesh Fraction of Low Vitrinite Reflectance Coals at 1273 K**

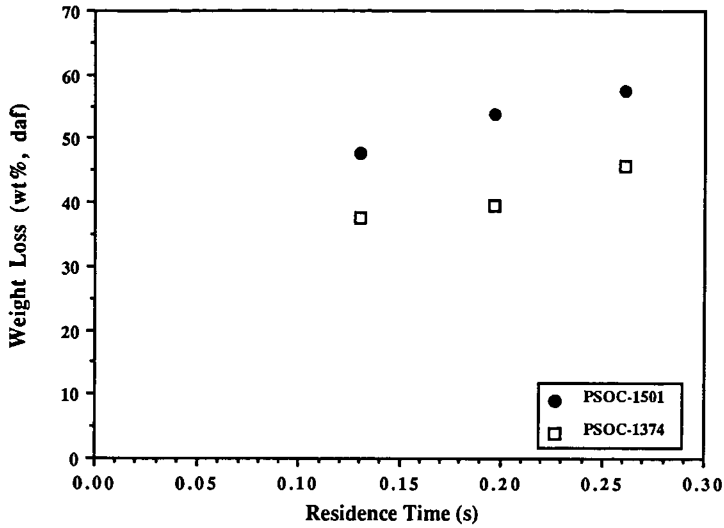


**Figure 5. Effect of Vitrinite Reflectance on Weight Loss During Combustion of 140x200 Mesh Fraction of Vitrinite-Rich Coals at 1073 K**

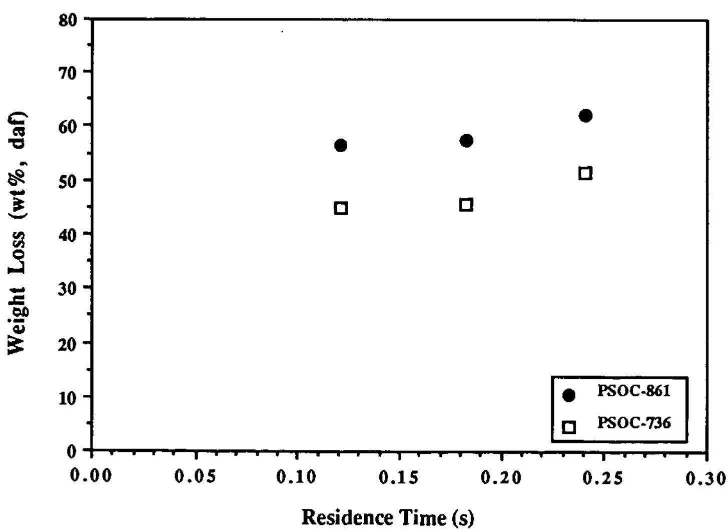


**Figure 6. Effect of Vitrinite Reflectance on Weight Loss During Combustion of 100x140 Mesh Fraction of Inertinite-Rich Coals at 1273 K**

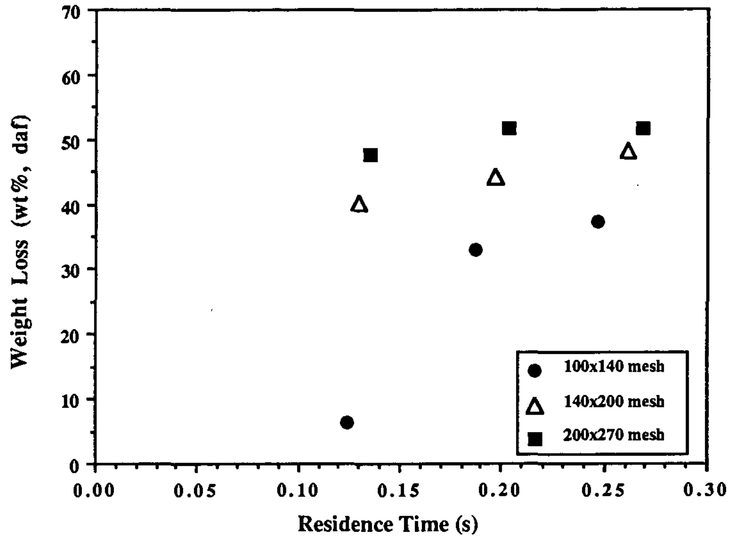


**Figure 7. Effect of Particle Size on Weight Loss for Intermediate Coal (PSOC-733) During Combustion at 1073 K**

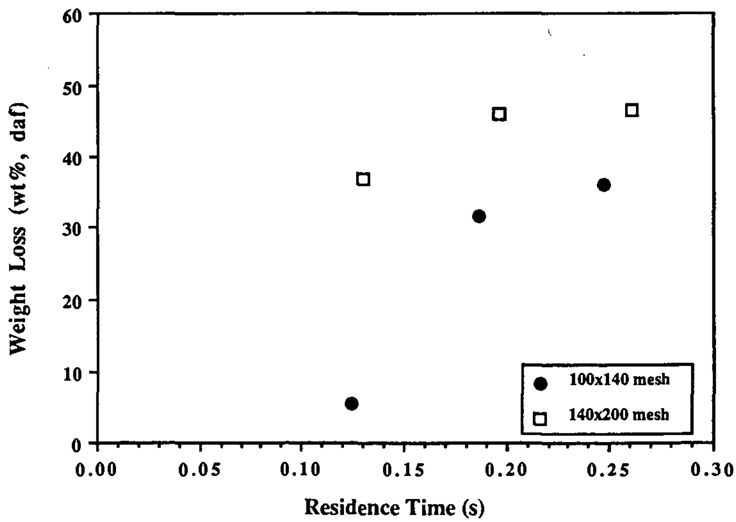


**Figure 8. Effect of Particle Size on Weight Loss for Inertinite-Rich Coal (PSOC-736) During Combustion at 1073 K**

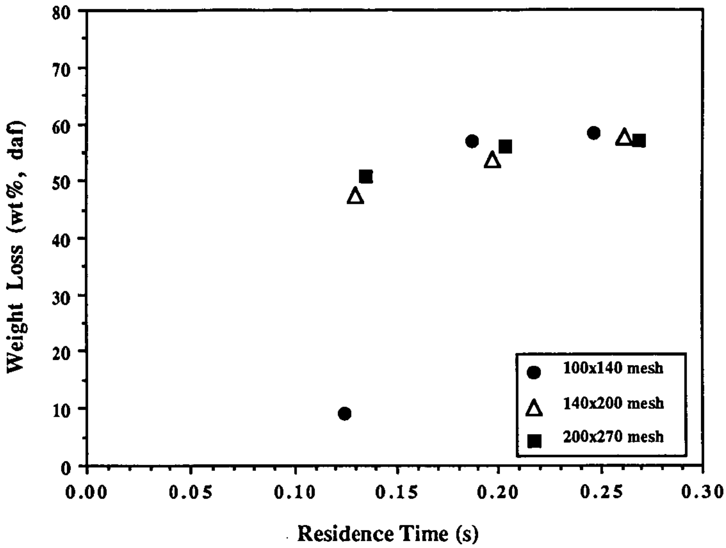


**Figure 9. Effect of Particle Size on Weight Loss for Vitrinite-Rich Coal (PSOC-1501) During Combustion at 1073 K**

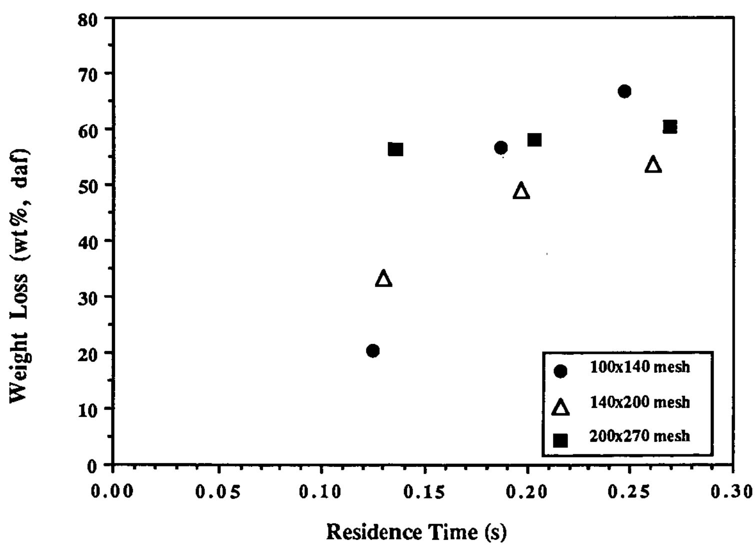


**Figure 10. Effect of Particle Size on Weight Loss for Liptinite-Rich Coal (PSOC-296) During Combustion at 1073 K**